

The Silver-Alkene Interaction as a Supramolecular Synthons; Divinylbenzene-based Assemblies.

Jennifer Burgess, Justine R. A. Cottam, and Peter J. Steel*

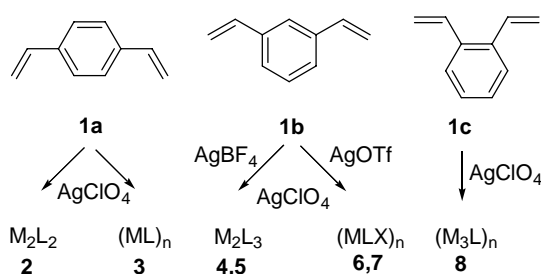
Department of Chemistry, College of Science, University of Canterbury, Christchurch 8020, New Zealand

Email: peter.steel@canterbury.ac.nz

Metall-supramolecular chemistry involves the use of bridging organic ligands and metal ions for the construction of discrete and polymeric assemblies with diverse molecular architectures.¹ By far the most commonly employed bridging ligands are those that contain nitrogen heterocycles, such as pyridine rings, as the sites for metal binding.^{1,2} Of the various metals used, silver(I) salts have proved particularly popular in recent years, as this d^{10} metal ion offers particularly versatile coordination requirements and readily binds to nitrogen heterocycles, as well as to ligands having oxygen, phosphorus, sulfur and other common donors.³

Silver(I) has long been known to interact with carbon-carbon double bonds,⁴ a fact which has routinely been exploited in the chromatographic separations of alkene mixtures,⁵ in NMR shift reagents for alkenes⁶ and for the preparation of solid derivatives of olefinic hydrocarbons for structural characterization.⁷ However, the silver-alkene interaction has not been systematically investigated as a synthon for supramolecular chemistry. We now describe the self-assembly of both discrete and polymeric species formed from reactions of silver(I) salts with the three isomers of divinylbenzene, in which these dienes act as bridging ligands with η^2 -coordination of the vinyl groups.

Scheme 1



Each of the isomeric divinylbenzenes⁸ was reacted with various silver(I) salts under a range of experimental reaction conditions, the results of which are schematically presented in Scheme 1. Reaction of silver perchlorate with *para*-divinylbenzene (1a) furnished two products, (2) and (3), each of which had 1:1 metal:ligand stoichiometry. X-Ray crystal structure determination⁹ revealed that complex 2 is an M_2L_2 metallomacrocyclic, in which two silver atoms are bridged by two *para*-divinylbenzene ligands, with η^2 -coordination by the vinyl groups and additional weaker interactions with monodentate perchlorate anions (Figure 1). Such a discrete M_2L_2 species is exactly that expected to be thermodynamically most stable for a 1:1 ratio of (non-chelating) bridging ligands and silver atoms, on the basis of enthalpic and entropic considerations. On one occasion a second complex, 3, was obtained, the crystals of which

were highly unstable. Although a full structure determination proved elusive, we were able to ascertain¹⁰ that this compound was a 2D metallopolymer, in which 1:1 *para*-divinylbenzene:silver zigzag chains were cross-linked by coordinated acetone molecules.

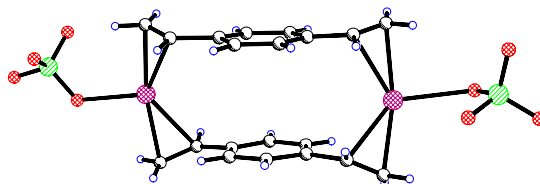


Figure 1. X-Ray structure of the discrete M_2L_2 complex 2.

Reactions of *meta*-divinylbenzene (1b) also provided both discrete and polymeric assemblies. The product (4) from reaction with silver tetrafluoroborate in dichloromethane solution was found^{9,11} to have a discrete M_2L_3 cage-like structure (Figure 2), within which three *meta*-divinylbenzene ligands bridge two trigonally coordinated silver atoms. All three *meta*-divinylbenzene ligands are planar and display a (non-helical) propeller-like arrangement when viewed from above. The tetrafluoroborate anions are non-coordinated. The product (5) from reaction with silver perchlorate in methanol solution proved to be isomorphous but not quite isostructural.⁹ In this case one of the two silver atoms within the trigonal prismatic cage was found to experience some pyramidalization as a result of a stronger interaction with the adjacent perchlorate counterion.

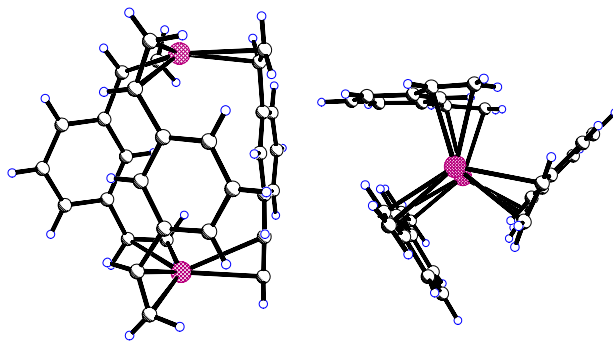


Figure 2. Side and top views of the X-ray structure of the discrete M_2L_3 complex 4.

A similar reaction of *meta*-divinylbenzene with silver perchlorate in toluene solution furnished a completely different product, (**6**), that was found to be polymeric. This compound⁹ consists of 1D chains of silver atoms bridged by both η^2 -coordinated *meta*-divinylbenzene ligands and bidentate perchlorate anions (Figure 3, top). A related assembly (**7**) was also formed from reaction of this ligand with silver triflate in THF solution. However, in this case the structural characterization⁹ was somewhat more intriguing, in that the complex crystallized with three independent silver atoms in the asymmetric unit with only half the triflate anions bridging the silver centers (Figure 3, bottom).

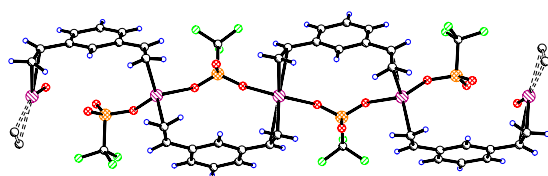
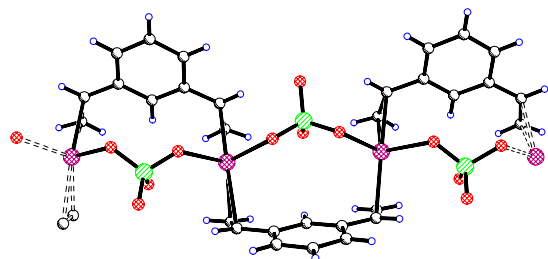


Figure 3. X-Ray structures of sections of the polymeric (MLX)_n complexes **6** (top) and **7** (bottom).

The product (**8**) from reaction of *ortho*-divinylbenzene (**1c**) with silver perchlorate proved to be even more interesting. In this case the ligand was found⁹ to bond to three silver atoms, *via* the two vinyl groups, as observed above, but also through the benzene ring, as has commonly been reported for various benzenoid aromatic hydrocarbons.¹² The three silvers all coordinate to the same face of the ligand (Figure 4). The full structure of the resulting assembly proved to be rather complex. Figure 4 also shows how bridging water molecules serve to interconnect the units into a 2D array. Not shown is the fact that the perchlorate counterions also act as bridges to result in a 3D network.

In conclusion, we have shown that the silver-alkene interaction represents a useful synthon for the construction of both discrete and polymeric metallosupramolecular architectures. The vinyl groups employed in this study experience η^2 -coordination, with Ag-C distances in the range 2.345–2.704 Å. In all cases the Ag-C bond distance to the terminal carbon of the vinyl group is shorter than that to the other carbon. Studies extending this design concept to more complex cases, including chiral examples, are currently underway.

Acknowledgment. We thank the Royal Society of New Zealand Marsden Fund for financial support.

Supporting Information Available: Crystallographic data for compounds **2–8**.

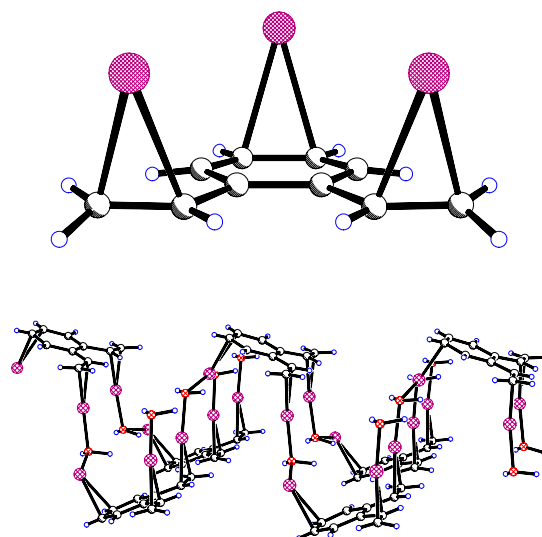


Figure 4. X-ray structure of the polymeric (M₃L)_n complex **8** showing coordination of the three silver atoms to the same face of the ligand (top) and the 2D array resulting from water bridging (bottom).

- (1) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853–908. (b) Swiegers, G. F.; Malefetse, T. J. *Chem. Rev.* **2000**, *100*, 3483–3537. (c) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629–1658. (d) Johnson, D. W.; Raymond, K. N. *Supramol. Chem.* **2001**, *13*, 639–659. (e) Holliday, B. J.; Mirkin, C. A. *Angew. Chem. Int. Ed.* **2001**, *40*, 2022–2043. (f) Siedel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972–983. (g) Würthner, F.; You, C.-C.; Saha-Möller, C. R. *Chem. Soc. Rev.* **2004**, *33*, 133–146. (h) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373–399. (i) Thanasekaran, P.; Liao, R.-T.; Liu, Y.-H.; Rajendran, T.; Rajagopal, S.; Lu, K.-L. *Coord. Chem. Rev.* **2005**, *249*, 1085–1110. (j) Hosseini, M. W. *Acc. Chem. Res.* **2005**, *38*, 313–323.
- (2) (a) Gavrilova, A. L.; Bosnich, B. *Chem. Rev.* **2004**, *104*, 349–383; (b) Steel, P. J. *Acc. Chem. Res.* **2005**, *38*, 243–250.
- (3) (a) Hartshorn, C. M.; Steel, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 3927–3934. (b) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Adv. Inorg. Chem.* **1999**, *46*, 173–303. (c) Khlobystov, A. N.; Blake, A. J.; Champness, N. R.; Lemenovskii, D. A.; Majouga, A. G.; Zyk, N. V.; Schröder, M. *Coord. Chem. Rev.* **2001**, *222*, 155–192; (d) Zheng, S.-L.; Tong, M.-L.; Chen, X.-M. *Coord. Chem. Rev.* **2003**, *246*, 185–202. (e) Chen, C.-L.; Kang, B.-S.; Su, C.-Y. *Aust. J. Chem.* **2006**, in press.
- (4) (a) Winstein, S.; Lucas, H. J. *J. Am. Chem. Soc.* **1938**, *60*, 836–847. (b) Bennett, M. A. *Chem. Rev.* **1962**, *62*, 611–652.
- (5) (a) Williams, C. M.; Mander, L. N. *Tetrahedron* **2001**, *57*, 425–447. (b) J. Kaneti, J.; de Smet, L. C. P. M.; Boom, R.; Zuñihof, H.; Sudhölter, E. J. R. *J. Phys. Chem.* **2002**, *106*, 11197–11204.
- (6) Beverwijk, C. D. M.; van Dongen, J. P. C. M. *Tetrahedron Lett.* **1972**, *13*, 4291–4294.
- (7) See, for example: Jackson, R. B.; Streib, W. E. *J. Am. Chem. Soc.* **1967**, *89*, 2539–2543.
- (8) The divinylbenzenes were prepared from the corresponding bis(bromomethyl)benzenes by Wittig reactions, using an adaptation of the following procedure: Carreno, M.; Hernandez-Sanchez, R.; Mahugo, J.; Urbano, A. *J. Org. Chem.* **1999**, *64*, 1387–1390.
- (9) Summary of X-ray details: **2**: C₂₀H₂₀Ag₂Cl₂O₈, monoclinic, P2₁/c, Z = 4, wR₂ (all data) = 0.1037, R₁ [I > 2σ(I)] 0.0388; **4**: C₃₀H₃₀Ag₂B₂F₈, monoclinic, P2₁/n, Z = 8, wR₂ (all data) = 0.1349, R₁ [I > 2σ(I)] 0.0543; **5**: C₃₀H₃₀Ag₂Cl₂O₈, monoclinic, P2₁/n, Z = 8, wR₂ (all data) = 0.1229, R₁ [I > 2σ(I)] 0.0500; **6**: C₁₀H₁₀AgClO₄, monoclinic, P2₁/c, Z = 4, wR₂ (all data) = 0.0530, R₁ [I > 2σ(I)] 0.0213; **7**: C₂₂H₂₁Ag₂F₆O₆S₂, monoclinic, C2/c, Z = 8, wR₂ (all data) = 0.1145, R₁ [I > 2σ(I)] 0.0461; **8**: C₁₀H₁₄Ag₃Cl₃O₁₄, orthorhombic, Pnma, Z = 4, wR₂ (all data) = 0.1083, R₁ [I > 2σ(I)] 0.0364.
- (10) Despite several attempts, only a partial dataset was able to be collected for this unstable compound. However, this was sufficient to reveal the structure.
- (11) Remarkably, this compound was also isolated as the sole product from the reaction of silver tetrafluoroborate with a commercial sample of a mixture of all three isomers of divinylbenzene.
- (12) Munakata, M.; Wu, L. P.; Ning, G. L. *Coord. Chem. Rev.* **2000**, *198*, 171–203.
